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National Aeronautics and Space Administration

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN ATOMS AT
TEMPERATURES BELOW 100° K

by

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J. H. Wilson

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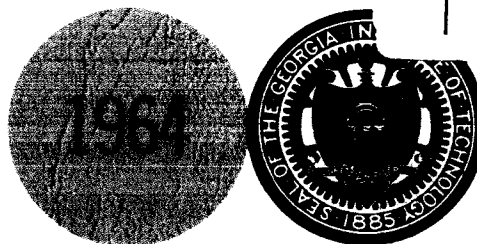
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Project A-661

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.	1
II. CURRENT STATUS OF RESEARCH.	2
A. Ionization and Appearance Potential Measurements.	2
B. Cryogenic Purification and Mass Spectrometer Inlet System .	4
C. Preparation of Diatomic Species of the Alkali Metals. . . .	5
D. Reactions of Atomic Hydrogen.	8
E. Furnace Beam Inlet System	10
III. PLANS FOR NEXT REPORTING PERIOD	18

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Schematic of Furnace Beam Inlet System.	12
2	Gas Injection and Pumping Arrangement for the Furnace Beam Inlet System.	16

LIST OF TABLES

	<u>Page</u>
Table I. Appearance Potentials.	4

I. INTRODUCTION

There are several problems within the broad area of chemical reactivity at cryogenic temperatures that are to be examined during the course of this investigation. In the order of their performance in a typical experiment, these include (1) generation of suitable reactants or precursors, (2) low temperature reactions, (3) purification of products, and (4) identification and characterization, by their elementary physical and chemical behavior, of selected product substances. A few sentences on each of these problems will serve to introduce the technical discussion in succeeding chapters of this report.

(1) Very few substances will react upon contact at cryogenic temperatures,¹ but rather most require some manner of activation. In these studies we are concentrating on two schemes of activation for the generation of suitable precursors, i.e., electrodeless glow discharge and pyrolysis.

(2) The reactor designs have been such as to quench or trap some species from the above activation process, or to react the effluent from the activation process with a second substance which is already in a cold reactor.

(3) Purification techniques using continuous fractional sublimation and recondensation which we call "thermal chromatography" are being developed. Presumably adsorption and absorption schemes also are possibilities.

(4) Identification of product substances is accomplished mass spectrometrically utilizing a cryogenically cooled sample inlet system. The mass spectrometer is also used to follow the chemistry occurring during warm-up as well as to measure the appearance potentials and ionization potentials of species of interest, usually to within an accuracy of ± 0.1 ev.

¹ McGee, H. A. Jr., and Martin, W. J., Cryogenics 2, 257 (1962).

The motivation for the choice of systems to study is based on considerations from space chemistry. For example, it is now generally realized that any real understanding of chemical processes occurring on certain objects of astronomical interest, must be realized in terms of cryochemistry. As immediate examples of this, one may recall the "dirty snowball" model of comets and the atmospheric chemistry of the Jovian planets.

A rather broad literature review including many experiments in cryochemistry and containing over 200 references has been prepared by McGee and Martin.¹ It is our objective to restudy and to expand upon some of these earlier observations of chemical reactivity.

II. CURRENT STATUS OF RESEARCH

A. Ionization and Appearance Potential Measurements

The experimental determination of ionization potentials is important for the numbers are useful in thermochemistry, in kinetics, and other areas of chemistry and chemical physics. More specifically, for the case of the unusual chemical behavior at very low temperatures that is of concern here, the data may be applied to identification problems, to molecular structure problems and to unusual chemical kinetic problems.

Our procedure for the experimental determination of the appearance and ionization potentials employs the Fox retarding potential difference (RPD) method and has been described in detail in earlier reports.² This method is well suited for use with the Bendix T-O-F mass spectrometer and is generally thought to be the most accurate method available for the measurement of appearance potentials

² McGee, H. A. Jr., Second Semiannual Technical Report, Grant NsG-337, March 1, 1964.

by electron impact techniques without going to very elaborate techniques to produce monochromatic beams.

In our continuing study of carbene, CH_2 , and its dihalo derivatives, we have examined several molecules as possible parents for the production of CF_2 and Cl_2 . We are interested in the energetics of the carbenes, and hence potential measurements are most valuable in that one can then deduce heats of formation, bond energies and make reasonable arguments about stabilities. Energetic considerations then aid in understanding the observed low temperature chemical behavior of the carbenes.

We have examined the equilibrium decomposition of C_2I_4 , CHI_3 , CHClF_2 , CF_2ClCOOH and ClF_3 at temperatures of up to 500°C . The decomposition was conducted in a line-of-sight furnace attached to the mass spectrometer in an assembly which has been described in previous reports. None of these compounds produced detectable amounts of the desired CX_2 species. An inlet system has recently been constructed which permits the parent compounds to be passed over a heated filament immediately before the gas enters the mass spectrometer ionization chamber.³ The filament temperature is determined by an optical pyrometer. A grid upon which can be impressed a potential bias has been placed between the filament and the ionization region of the spectrometer. A positive bias on this grid prevents the passage into the mass spectrometer of ions that have been produced by surface ionization on the hot filament. The compounds listed below and several others, such as CF_2CFCl and cyclo- C_4F_8 , are being examined at the higher temperatures which can be attained with the heated filament.

³ Much of the earlier work on heated filament decompositions has been reviewed by Lossing in Mass Spectrometry, C. A. McDowell, editor, McGraw-Hill, New York, 1963.

The results are usually quite different from those obtained from the earlier equilibrium furnace decompositions.

The several electron impact potentials that have been measured are listed in the following table. Most of these are previously unreported.

TABLE I
APPEARANCE POTENTIALS

<u>Ion</u>	<u>Parent</u>	<u>Measured A. P.</u>	<u>Literature A. P.</u>
CF_3I^+	CF_3I	$9.4 \pm 0.1 \text{ e.v.}$	
CF_3^+	CF_3I	10.2 ± 0.1	
CHI_3^+	CHI_3	9.45 ± 0.1	
CHI_2^+	CHI_3	10.2 ± 0.1	
CHClF_2^+	CHClF_2	Approx. 12.3	12.69 ± 0.15
CHF_2^+	CHClF_2	Approx. 12.8	12.59 ± 0.15
CF_2^+	CF_2ClCOOH	13.4 ± 0.1	
CF_2^+	C_2F_4	Approx. 15	15.2 ± 0.2

B. Cryogenic Purification and Mass Spectrometer Inlet System

Every chemist is familiar with the bands of deposits that may be found in a cold trap on a vacuum rack when mixtures of substances are passed through it. This effect is particularly noticeable when the dewar around the trap is only partially full of refrigerant (i.e., when there is a thermal gradient in the trap). The objective of the purification system being developed is to impress such a gradient upon a long tube, to carefully control the gradient, and to use

it as a somewhat crude separative procedure. We have called this arrangement "thermal chromatography." In addition, the coldest end of this tube upon which any desired gradient may be impressed is provided with a capillary leak such that the vapor in the cold end of the tube is bled into the ion source of a time-of-flight mass spectrometer. The physical arrangement is such that this vapor is in no way heated above the operating temperature of the cold end of the gradient tube before it is ionized in the electron beam of the ion source. This device has been described in detail in earlier reports.²

As working substances for use in the development of the cryogenic inlet system, it was desirable to use materials that were typical of those resulting from synthesis procedures with cryogenic reactors, but which were also materials about which most information was already available from previous investigations. This latter point was particularly troublesome since there is so very little known about any low temperature system. However, the oxygen fluorides seemed to best fill all requirements. O_3F_2 begins to decompose at $90^\circ K$, O_2F_2 at $173^\circ K$, and neither exists at temperatures of as high as room temperature. To the present time, only admittedly crude spectra have been obtained, but it is clear that O_2F_2 and O_3F_2 have been successfully transferred from the reactor in which they were synthesized into the inlet arrangement, and their spectra are consistent with the structures FOOF and FOOF₂ respectively. Both molecules have parent peaks, and both molecules have positive heats of formation of 4.73 ± 0.3 Kcal/mole and 6.24 ± 0.75 Kcal/mole respectively.⁴

C. Preparation of Diatomic Species of the Alkali Metals

Sodium is one of the more prominent species present in tables of cosmic

⁴ Amster, A. B., Neff, J. A., and Aitken, A. J., final report on contract NASr-38, Nov. 1, 1962, Stanford Research Institute.

abundances. Emission from the atom appears in comet head spectra at about 1 A.U. It is also interesting that the vapor over the liquid at its normal boiling point is 17 mole per cent Na_2 . This species increases in concentration in the equilibrium saturated vapor with increasing temperature. It has a $^1\Sigma$ ground state and would presumably behave chemically rather like the diatomic species of the first alkali metal, H_2 .

We are investigating the low temperature stability of Na_2 in an apparatus that has been described in previous reports. This program is receiving a very minimum of support from NsG-337,^a but it has seemed reasonable to keep NASA informed of the progress.

The major problems at present are the design of the cell in which the sodium is boiled and the technique of loading very pure sodium into the cell in a way not allowing contamination. The cell is machined from stainless steel type 446 (27 Cr, remainder essentially all Fe). Preliminary runs have indicated that this material is suitable for use in sodium atmospheres at temperatures at least up to the normal boiling point (833°C).

The cell was suspended in an evacuated quartz tube by hangers made of 3/32 in. diameter fused quartz rods. This eliminated the problem of heat loss by conduction in the hangers, as well as heat generation by coupling of the induction heater which would have occurred with metal hangers.

The flow rate of the sodium from the cell is controlled by the size of an orifice which was initially drilled with a 0.0035 in. diameter twist drill. The first runs indicated that this permitted a much too rapid sodium flow rate. The flow rate of N_2 gas through the orifice was measured by water

^a The cumulative expenditures have been less than \$1000.

displacement as approximately 6.6 gm/hr. This is about an order of magnitude faster than desired for efficient quenching of the sodium vapor. Calculations indicate that an orifice diameter of approximately 0.0015 in. would give an acceptable flow rate. Two methods of obtaining an orifice of this approximate size have been tried; (1) electron beam drilling and (2) indenting the metal with a sharp needle followed by polishing on the back side until a hole is produced. This latter technique has worked very well. The desired orifice has also been drilled with a Hamilton Zeiss model WI-2, 3 KW electron beam welder located at the Marshall Space Flight Center in Huntsville, Alabama. This technique has not worked well. The manufacturer guarantees an electron beam focus down to 0.005 in., and it seems to be possible to get 0.002 in. to 0.003 in. holes on occasion, but not in a reproducible manner.

A Lepel high frequency induction heater (2.5 KW output) is being used to heat the cell. This machine has proved very satisfactory for bringing the cell up to the normal boiling point in about 2 min. and controlling the temperature within about 2 degrees centigrade. At the normal boiling point, the screwed cap on the cell seemed to run rather consistently 20° C below the main cell temperature. The major problem experienced in heating the cell has resulted from the fact that the stainless steel is ferro-magnetic. Ferro-magnetic materials become para-magnetic at the Curie point (approximately 768° C). This transition drastically changes the electrical characteristics of the load and causes very rapid changes in the plate and grid currents of the induction heater. The heater has an automatic overload relay switch which stops the machine when the currents get out of specified ranges and a time delay prevents its immediate restarting. To approach the ideal of a smooth, rapid heat, the cell was brought

up to the Curie point by intermittent heating with short but rapidly repetitive bursts of power.

Various coils have been used with the heater, with an 8 turn coil of 3/16 in. diameter copper tubing, having an O.D. of 2-1/4 in. and a length of 3-1/2 in. appearing to be about optimum. Coils with fewer turns resulted in the power output being too low.

In attempts to load pure sodium, both an ordinary glove box and a plastic collapsable glove box have been used. The enclosures are purged with dry nitrogen. However, in both enclosures, upon cutting the sodium, the shiny surface is immediately seen to take on a gray oxide coating. In preliminary runs, the decomposition of NaN_3 ($2\text{NaN}_3 \rightarrow 2\text{Na} + 3\text{N}_2$) has also proven to be troublesome. Vacuum distillation, followed by direct loading of the cell under vacuum on the vacuum rack is now being investigated. This seems to be the most promising technique.

D. Reactions of Atomic Hydrogen

The basic system for reacting hydrogen, oxygen or nitrogen atoms with simple molecules of carbon, hydrogen, nitrogen and oxygen at temperatures below 100°K has been built and is now operable.

Only one significant change from the design presented in the previous technical report has been made. This difference is a change in the position of the radio frequency discharge coil used to produce the atomic species. The discharge coil is now positioned externally, i.e., not inside the reactor itself as previously shown, but on the vertical part of the glass manifold 55 cm above the reactant liquid level in the glass reactor. The discharge coil is connected

in series with a capacitor having a variable range of 100-1100 μ pf. Using this arrangement, a frequency range of 3.0 to 5.4 mc is obtainable.

The hydrogen discharge is ignited with the aid of a Tesla coil when necessary. To prevent extinction of the discharge due to increasing hydrogen flow rate, a small circular glass tube was put inside the top region of the discharge tube. The circular tube causes the entering hydrogen to flow in a swirling motion through the discharge region and the hydrogen is therefore present for a longer time in the discharge region. The plasma is also less likely to be extinguished by a brisk mass flow through the discharge region sweeping out too many of the ions. The discharge tube is cooled by air jets.

The bright crimson hydrogen discharge can be sustained to a pressure of up to about 800 μ Hg. A less bright hydrogen discharge occurs at higher pressures, and this glow can be sustained to about 4 mm Hg. A better matching of the impedance of the discharge to that of the transmitter, which is now underway, will hopefully yield a more intense discharge.

In initial experiments, atomic hydrogen is being reacted with solid nitric oxide at 77° K. Due to impurities in the nitric oxide or in the reaction system, the first experiments have been inconclusive. Pure solid nitric oxide is blue-white, but the solid nitric oxide we have been using is a mixture of blue-white and green materials. Several purification procedures are being investigated.

Liquid solutions of nitric oxide and propane at 90° K are also to be reacted with atomic hydrogen. At 90° K, concentrations of less than 0.18 mole fraction nitric oxide in propane should produce miscible solutions. In making the solubility calculations, the lack of ideal solution behavior was considered by using Hildebrand's solubility parameter.⁵

⁵ Hildebrand, J. H., and Scott, R. L., The Solubility of Nonelectrolytes, Reinhold Publishing Corp., 1950.

At 90° K, a 0.18 mole fraction solution of nitric oxide in propane has a calculated vapor pressure of 580 μ Hg, and since, the present discharge coil arrangement can be used to produce hydrogen atoms at pressures greater than this, it is possible to pump the gas containing the atoms into the reactor containing the cold solution.

In all studies, the reaction products are identified by use of the time-of-flight mass spectrometer. The reaction products are transferred from the glass reactor to the cold inlet system by use of the liquid nitrogen cooled pipet system described previously.

E. Furnace Beam Inlet System

Many species of interest in studies of chemical problems in astronomy may be conveniently made by the heterogeneous reaction of a gas with a solid film. It may also be necessary or convenient to activate the impinging gas phase to produce say atomic hydrogen, just ahead of its contacting the solid film. For the purpose of the present studies, it is not considered satisfactory to merely trap the effluent from such a heterogeneous reaction and to then identify the various end products by one of several standard procedures, perhaps by chromatography. But rather, we wish to detect the initially formed species in the reaction which may themselves be transitory or highly reactive. After the nature of the effluent is accessed as a function of temperature, pressure, flow rate, etc., the experiment will usually involve a quenching of this gas to cryogenic temperatures. The objective of this latter step is, of course, to study the low temperature stability and reactivity of species, transitory at ordinary conditions, but perhaps quite stable at cryogenic temperatures.

To accomplish the first phase of this program it has been necessary to design and construct a flow system with a furnace arrangement such that a sample of the effluent from the furnace may be leaked continuously into the ion source of the mass spectrometer. This inlet system must be a collisionless, molecular beam type, since the species that one wishes to detect are often transitory. Such inlet arrangements were first used by Eltenton⁶ and subsequently highly developed by Lossing,⁷ Dibeler⁸ and others.⁹ The arrangement that has been built here is similar in some ways to these earlier designs, but it also has certain design features peculiar to our particular interests.

The apparatus is shown schematically in Figure 1. The main parts are a 3/8 in. O.D. furnace tube [1]* through which the gas sample is admitted, a 1-1/2 in. O.D. exhaust tube [2] which contains the furnace tube and acts as a pumpout tube and cooling tube for the gas from the furnace, and a 4.5 in. O.D. piston [3] which moves in a double O-ring gland into a vacuum lock and which is connected to a 3 in. O.D. extension can [4] that moves to within 3/16 in. of the ion grids of the mass spectrometer. In operation, the gas sample travels down the furnace tube, is heated by a 2-1/2 in. length of nichrome wire wound furnace [5] (whose upper temperature limit is approximately 1000° C), and impinges on a platinum foil [6] which is mechanically sealed into the end of the exhaust tube and, in addition, is cooled by a stainless steel cooling coil [7] about the exhaust tube. The 0.006 in. thick platinum foil containing a hole

⁶ Eltenton, G. C., J. Chem. Phys. 15, 455 (1947).

⁷ Lossing, F. P., Marsden, D.G.H., and Farmer, J. B., Can. J. Chem. 34, 701 (1956).

⁸ Herron, J. T., and Dibeler, V. H., J. Research Nat. Bur. Standards, 65A, 405 (1961).

⁹ An excellent review is contained in Mass Spectrometry, C. A. McDowell, editor, McGraw-Hill, New York, 1963.

* Numbers in brackets correspond to numbers on figures.

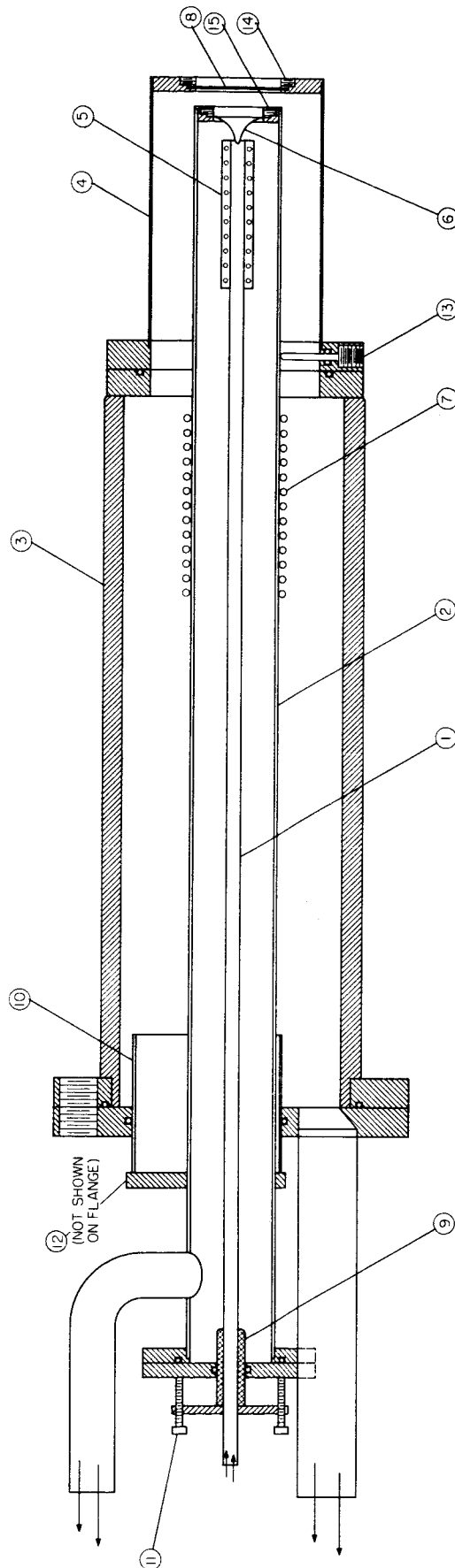


Figure 1. Schematic of Furnace Beam Inlet System.

of 0.004 in. diameter allows a jet of the gas to be admitted into the intermediate pumping space. The foil is nipple shaped to allow the orifice, in the deepest point of the nipple, to extend into the furnace region and consequently to be at approximately the same temperature as the gas from the furnace. The intermediate pumping space, which is that volume within the piston and extension can and outside of the exhaust tube, is pumped out by a diffusion pump to a pressure of approximately 10^{-3} to 10^{-4} mm Hg. The jet of gas from the platinum foil then strikes a 0.010 in. thick stainless steel disk [8] which contains a hole of 0.0135 in. diameter. This second disk is located within about 2 to 3 cm of the electron beam and serves to collimate the jet of gas from the platinum foil. Under the conditions of pressure in the intermediate space and assuming the gas leaving the platinum foil is at approximately the same temperature as the furnace, we expect that molecular flow is experienced through the final disk and therefore the mass spectrometer will essentially be recording the condition of the reactant gas as it exists in the furnace.

There are several features included in the design of the apparatus which provide for flexibility and convenience in operation and maintenance of the system. For instance, the furnace tube and exhaust tube are mounted through flanges by sleeves [9] and [10] which are free to slide in O-ring seals. By means of adjusting screws on the tubes [11] and [12] the distance between the end of the furnace tube and the platinum foil may be varied as may the distance between the platinum foil (which as mentioned previously is sealed into the end of the exhaust tube) and the steel disk in the bottom of the extension can. It is hoped that by adjusting these distances we will find

that we obtain an optimum sample beam for admission into the spectrometer. Also, for alignment of the two holes in the platinum and the steel disks, 3 positioning screws [13] are provided which come in through O-ring seals in the flange on the extension can at right angles to the exhaust tube and bear on the exhaust tube. The alignment of the two holes may be confirmed by shining a light into the furnace tube and observing from the opposite end a beam of light upon correct alignment. Obviously, this is done when the apparatus is withdrawn from the spectrometer. An attachment with a plexiglass window has been fabricated which allows one to evacuate the apparatus and then with the furnace at operating temperature to check the effect of the hot furnace upon alignment of the two holes. This attachment is identical to the compression nut [14] which holds the steel disk in place with the exception that a plexiglass window is cemented onto it, thus allowing for evacuation without insertion of the apparatus into the spectrometer.

Concerning the maintenance of the system, it is believed that plugging of the platinum foil by deposited solids may prove to be a problem. Therefore, the design is such that for removal and replacement or cleaning of the platinum foil, the apparatus may be withdrawn from the mass spectrometer, the steel disk compression nut and the disk itself removed from the outside, and then through the resulting opening, the platinum foil compression nut [15] and the foil removed. In an earlier apparatus the design was such that the entire system had to be disassembled for such an operation.

The flanges on the exhaust tube and the piston are provided with terminals for power and thermocouple connections. At present, the only power supplied to the system is to the furnace. However, in the future, experiments may be con-

ducted in which the incoming gas will be activated by passing it through an electrodeless discharge coil and the products of the discharge examined by passage into the spectrometer. In this case, the steel furnace tube is replaced by a quartz tube around which the discharge coil is placed. Thermocouple connections are made at present to the furnace, the platinum foil, the steel disk, and the wall just below the flange on the extension can. Additional thermocouple terminals are available should the need for other points of temperature measurement arise. The idea of a shielded thermocouple mounted directly in the gas stream within the furnace area is also being considered. However, the design of such a shielded thermocouple in so small a tube to give an accurate measure of the temperature of the gas appears to have its problems. As a first approximation, we will consider the gas to be at the same temperature as indicated by the thermocouple on the furnace. Also, the thermocouple on the platinum foil should allow us to draw some conclusions as to the accuracy of this approximation.

Figure 2 shows a simplified flow diagram of the experimental setup. Nitrogen [1] is used for flushing the system before and after the addition of the working gas [2]. The pressure gauge [3] upstream of the flow meter [4] is necessary for the determination of the flow rate of the input gas. The pressure at this point will normally be a few centimeters above atmospheric pressure. The leak valve [5] and the throttle valve [6] will be manipulated simultaneously to control the flow rate and the pressure, which may be varied from a few microns to several hundred millimeters of mercury. A Dubrovin vacuum [7] gauge is attached as closely as possible to the furnace tube to measure the system pressure. The pressure gauge [8] immediately downstream of

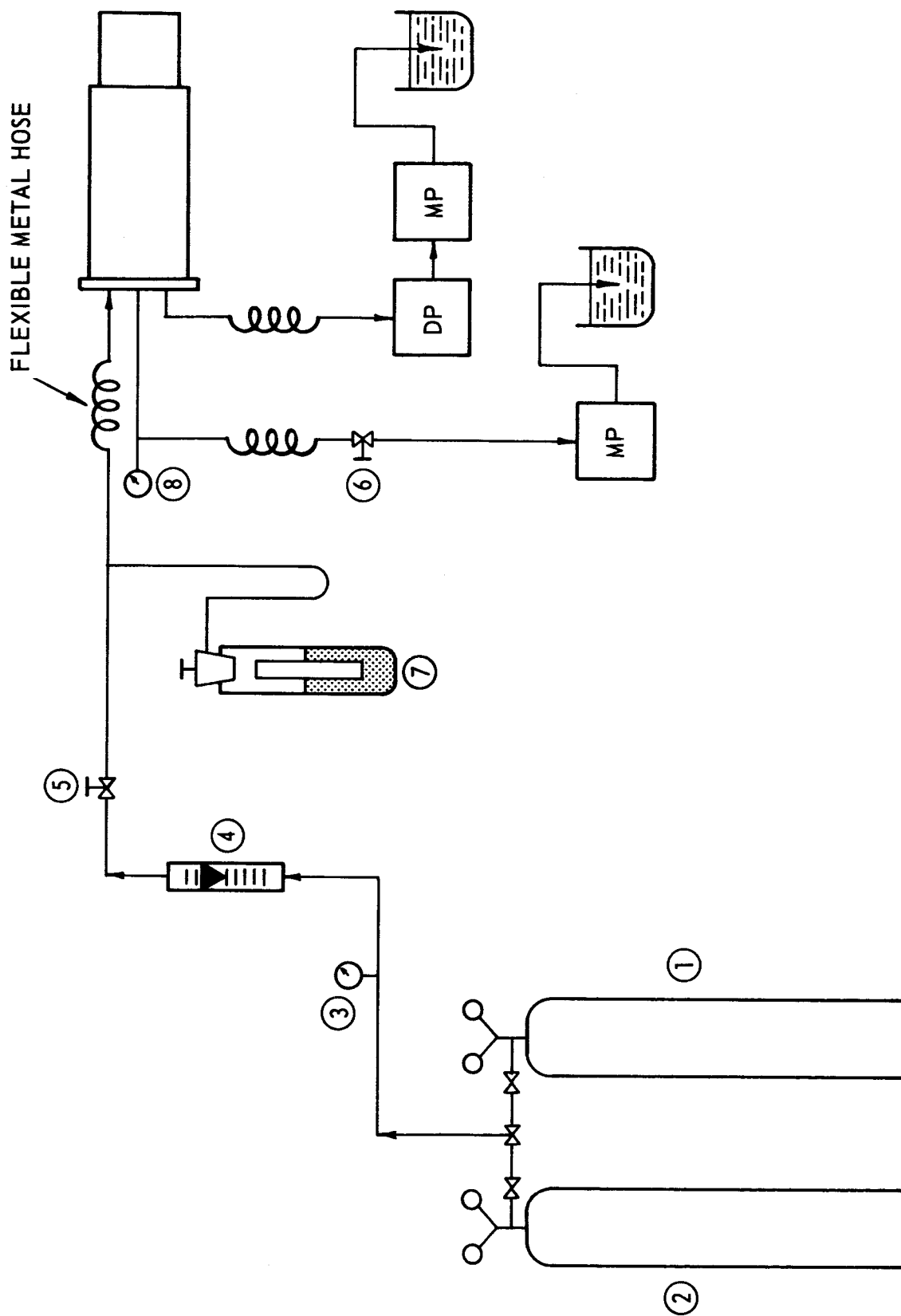


Figure 2. Gas Injection and Pumping Arrangement for the Furnace Beam Inlet System.

the furnace is used to give an indication of the pressure drop through the system and thus an indication of the accuracy of the Dubrovin gauge as a measure of the pressure in the furnace area. The exhaust gas is finally bubbled through an absorber to remove any toxic materials which may be present, and which one would not wish to exhaust into the room.

III. PLANS FOR NEXT REPORTING PERIOD

The work to be accomplished during the ensuing six months is categorized below under the same five major activities as used in discussing the "current status" in the preceding chapter. It appears that these activities will be almost completely experimental in contrast with the previous work which has been largely apparatus design and development.

(a) In the carbene work, CF_2 will be produced by pyrolysis on a hot filament in a flow system attached to the cryogenic purification and mass spectrometer inlet system. CF_2 is quite unreactive and is lost from the vapor phase only by diffusion to the walls. In our experiments this wall is the tube through which the gas is flowing and which has a linearly decreasing temperature in the direction of the flow. Our expectation is that at some point, i.e., at some low temperature, the CF_2 will condense on the wall as a stable entity. Then, by gentle warming, the CF_2 should begin to vaporize and its presence would again be apparent in the mass spectrum. The nature of these results will influence the continued work with carbene and its derivatives. The energy measurements will continue with emphasis on determining the ionization potential and heat of formation of CF_2 and Cl_2 .

(b) Mixtures of O_3F_2 and O_2F_2 will continue to be injected into the cryogenic mass spectrometer system. The functioning of the gradient tube, i.e., thermal chromatography, in separating these two molecules is being investigated. The existing crude mass spectra of these substances will be improved, and the ionization energy of each will be determined.

(c) Trapping experiments with sodium will continue. None of our previous experiments have utilized a matrix. The possible advantages of simultaneously condensing an inert material with the active material will be investigated.

(d) Reactivity studies of atomic hydrogen and nitric oxide, NO, will continue. The NO will in separate experiments be present as a gas, as a condensed solid film, and in a liquid solution. Rather old work has implied that HNO may be the major stable product of similar reactions. The cold product mixtures are here analyzed mass spectrometrically and hence the question of the existence of this species should be clarified.

(e) Thermal cracking experiments will be carried out in the new furnace beam inlet system to verify that it functions according to design, specifically that it allows one to monitor the composition of the effluent from the furnace itself. Some known system, probably $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$, will be used for this purpose. The first experiments will involve studies of the reaction of atomic hydrogen with solid films. This represents in many ways an instrumented version of the classic Paneth-Hofeditz mirror experiments. Similar work, but at lower temperatures, with the atomic hydrogen-carbon reaction has been recently described by Donn and Liner.¹⁰

¹⁰ Donn, B., and Liner, J., preprint of paper entitled, Temperature Dependence of the Heterogeneous Atomic Hydrogen Carbon Reaction, private communication, 1964.